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# Performance of close-coupled wave packet methods for molecule-corrugated surface scattering

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The  $\text{H}_2 + \text{LiF}(001)$  system was used to investigate the performance of the hybrid close-coupling wave packet (CCWP) method and of a symmetry adapted, fully close-coupled wave packet (SAWP) method for a molecule-surface problem characterized by fairly high corrugation. In the calculations, a realistic,  $\phi$ -dependent model potential was used. The calculations were performed for a collision energy of 0.2 eV, with  $\text{H}_2$  initially in its  $j=0$  rotational state at normal incidence to the surface. Large increases in the computational efficiencies of both wave packet methods were achieved by taking advantage of the potential coupling matrices associated with both methods becoming sparser with increasing molecule-surface distance. For the present model problem and employing this increased sparseness at longer range, the SAWP method is faster than the CCWP method by a factor of 2. The potential usefulness of the SAWP method for dissociative chemisorption problems is discussed. © 1995 American Institute of Physics.

## I. INTRODUCTION

Wave packet methods have been applied to a variety of molecule-surface scattering problems. Examples include the scattering of molecules from surfaces which contain impurities,<sup>1-3</sup> scattering from otherwise disordered surfaces,<sup>2,4,5</sup> atom-surface scattering involving phonon excitation,<sup>2,6</sup> rotationally<sup>2,7-16</sup> or vibrationally<sup>17</sup> inelastic molecule-surface scattering, and reactions on surfaces.<sup>18-33</sup>

Wave packet methods are also ideally suited for vector and parallel computers. As a result, in recent years much effort has been directed<sup>11,13,32,34-63</sup> at inventing wave packet techniques which are more efficient in terms of either computer time or central memory usage. The efficiency of a wave packet method depends on the number of basis functions used, the spectral range of the Hamiltonian, and the manner in which the Hamiltonian operations on the wave function are carried out.<sup>59,64</sup> Furthermore, recent work<sup>57,63</sup> has shown that in special cases the point-group symmetry of the crystal surface can be used to improve the efficiency of a wave packet method for molecule-surface scattering. Older work<sup>65</sup> had already shown how this can be done in the framework of the time-independent close-coupling method.<sup>66</sup>

The efficiency of performing the Hamiltonian operations depends to a large extent on the representation used for the wave function. One approach is to use a full close-coupling or variational basis representation (VBR)<sup>67</sup> for all degrees of freedom except the scattering coordinate.<sup>63</sup> A drawback of this method in its raw form is the unfavorable scaling of the potential energy operation with the number of basis functions  $N$  included in the coupled-channel expansion. The scaling is as  $N^2$ , the potential energy operation on the wave function becoming a matrix-vector product. An alternative approach<sup>58,59</sup> is to use a finite basis representation (FBR)<sup>67</sup> for all degrees of freedom. In this method, the potential energy operation is made cheaper by achieving a higher factorizability of this operation on the wave function. In particular,

the potential energy operation is performed by transforming the wave function from momentum space to coordinate space consecutively for each degree of freedom, followed by a simple multiplication in coordinate space, after which the wave function is transformed back to momentum space. Finally, hybrid methods exist, which use an FBR for some degrees of freedom and a VBR for the others. An example is the so-called close-coupling wave packet (CCWP) method,<sup>8,9</sup> which was the first wave packet method to be applied to molecule-corrugated surface scattering. The CCWP method employs an FBR for the diffractive degrees of freedom, while using a VBR or close-coupling representation for the molecular rotations.

In the original CCWP method, the potential energy operation scales with the number of rotational states  $N_{\text{rot}}$  included in the scattering basis set as  $N_{\text{rot}}^2$ . The scaling is with  $N_{\text{rot}}^{3/2}$  in the FBR method devised by Lemoine and Corey,<sup>58,59</sup> which would therefore seem to be more efficient. Their method has challenged us to come up with improvements to the existing CCWP method.

An obvious way to improve the efficiency of any hybrid or VBR wave packet method is to take advantage of the sparseness of the potential coupling matrix. In the CCWP method (VBR in rotational degrees of freedom only), the sparseness may result from certain coupling terms being zero over the entire range of the scattering coordinate accessible in the scattering. Clearly, this will be the case if a model potential is used which contains only low order rotational expansion terms. At larger values of the scattering coordinate, the sparseness may also result from certain coupling terms being relevant only at short range (close to the surface). This is certainly expected to be the case in molecule-surface scattering: The only spherical harmonics required to describe the long range  $C_3$  interaction of a homonuclear molecule with a surface are the  $Y_{00}$  and  $Y_{20}$  harmonics.<sup>68</sup>

The purpose of the present work is twofold. First, we

investigate to what extent the efficiency of the CCWP method can be improved by exploiting the sparseness of the potential coupling matrix. In the present research, we employ a realistic molecule–surface potential recently developed for  $\text{H}_2$  interacting with a  $\text{LiF}(001)$  surface.<sup>69,70</sup> At medium range and at long range the anisotropy of the potential is mostly contained in second order spherical harmonics, through the quadrupole-ionic lattice electrostatic interaction and the dispersion interaction. Close to the surface, higher order spherical harmonics in the potential expansion are also important, due to the short range repulsive interaction between  $\text{H}_2$  and the surface ions. In contrast to the Wolken potential for  $\text{H}_2 + \text{LiF}(001)$ ,<sup>66</sup> the new potential used here also depends on the azimuthal orientational angle  $\phi$  of the molecule.

Second, we investigate whether an even more efficient method can be obtained if a close-coupling representation is also used for the diffractive degrees of freedom, for the special case of normal incidence where the point-group symmetry of the crystal surface can be used to its maximum advantage. This work extends the application of the previously developed symmetry-adapted full close-coupling wave packet (SAWP) method<sup>63</sup> to problems in which the molecule surface potential also depends on the angle  $\phi$ , with the restriction presently that the initial magnetic rotational quantum number of the incident molecule is zero. Clearly, a full close-coupling method will only be efficient if only a few low-order diffraction (plane-wave) expansion terms are needed in the molecule–surface potential, or if higher order terms are important only close to the surface. The latter is known to be true for potentials constructed from pair interactions,<sup>71,72</sup> and model potentials used in calculations on elastic atom–surface scattering usually employ Fourier terms to order no higher than two.<sup>73–75</sup> Because the  $\text{LiF}(001)$  surface is a fairly corrugated surface, the  $\text{H}_2 + \text{LiF}$  problem represents a fairly severe test case in deciding whether a full close-coupling method can be made more efficient than the hybrid CCWP method, provided that a realistic model potential is used.

Developing a symmetry adapted treatment for normal incidence is relevant to the study of dissociative chemisorption: Many  $\text{H}_2$  + metal reaction systems obey “normal energy scaling”,<sup>76–78</sup> meaning that to a good approximation the measured reaction probabilities depend only on the kinetic energy associated with the translational motion normal to the surface. Of course, this dependence can then be obtained from calculations with normal incidence of the wave packet. At present, a major challenge in molecule–surface scattering is to perform a fully quantal six-dimensional (6D) wave packet calculation on the dissociative chemisorption of  $\text{H}_2$  on a low index copper surface. Accurate reaction barriers are available for  $\text{H}_2 + \text{Cu}$  from experiments,<sup>79</sup> and 6D wave packet calculations would constitute reliable tests of the multidimensional potential energy surfaces now being calculated for  $\text{H}_2$  interacting with low index copper surfaces using density functional theory.<sup>80–82</sup> The 6D reactive problem is the 5D inelastic problem augmented with the bond distance as an extra degree of freedom, and the symmetry adapted treatment we present here for  $\text{H}_2 + \text{LiF}(001)$  can be readily extended to dissociative chemisorption of  $\text{H}_2$  on  $\text{Cu}(100)$ .

The present paper is organized as follows. Section II presents the CCWP method and the SAWP method for normal incidence on a surface consisting of a square lattice. For both methods, we discuss how the sparseness of the potential coupling matrix maximum can be used to its maximum advantage on a vector computer. In Sec. III we show the improvement that can be obtained in both methods by employing sparseness, and compare the efficiencies of the improved CCWP method and the SAWP method. Section IV gives our conclusions.

## II. THEORY

In a previous paper,<sup>63</sup> the CCWP and SAWP methods were outlined and presented in considerable detail. In the present paper we will be more brief, except that now details are given concerning the methods used to employ the sparseness of the potential coupling matrix. Also, we describe how the transformation to a symmetry-adapted basis set for a homonuclear diatomic molecule scattering off a square lattice (including the  $\phi$  degree of freedom) can be effected. The general features of the wave packet methods used are described in Sec. II A. Details particular to the CCWP method are given in Sec. II B. A description of the SAWP method (including the transformation to the symmetry adapted basis set) is given in Sec. II C. The spectral range associated with both methods is discussed in Sec. II D. The essential features of the  $\phi$ -dependent model potential used in the present calculations are briefly discussed in Sec. II E. Section II F gives some numerical details concerning the calculations presented and discussed in Sec. III.

### A. Outline of wave packet methods

The Hamiltonian for a rigid rotor, diatomic molecule scattering off a static corrugated surface can be written

$$\hat{H} = -\frac{1}{2M} \nabla_{\mathbf{R}}^2 + H_{\text{rot}} + V(X, Y, Z, \theta, \phi), \quad (1)$$

where we used atomic units. In Eq. (1),  $M$  is the mass of the diatomic molecule,  $\mathbf{R} = (X, Y, Z)$  describes the position of the molecule,  $H_{\text{rot}}$  is the molecular rotational Hamiltonian, and  $V$  is the molecule–surface interaction potential which depends on  $\mathbf{R}$  and also on the molecular orientation angles  $\theta$  and  $\phi$  (see Sec. II E). The  $X$  and  $Y$  axes are parallel to the surface and lie along the direction of the lattice vectors (here we consider the case of a square surface unit cell), and  $Z$  is taken to be positive above the surface. The angles  $\theta$  and  $\phi$  are the polar and azimuthal angles defining the orientation of the molecular axis with respect to  $Z$  and  $X$ .

The solution to the time-dependent Schrödinger equation can be written as

$$\Psi(\mathbf{R}, \theta, \phi, t) = \exp[-i\hat{H}(t-t_0)]\Psi(\mathbf{R}, \theta, \phi, t_0), \quad (2)$$

where  $\Psi(\mathbf{R}, \theta, \phi, t_0)$  represents the initial state of the system. Equation (2) is an initial value problem, and to solve it we first define the initial wave function

$$\Psi(\mathbf{R}, \theta, \phi, t_0) = b(Z) \sqrt{1/(L_x L_y)} \exp[i\mathbf{K}_0 \cdot \mathbf{r}] Y_{j_0 m_{j_0}}(\theta, \phi) \quad (3)$$

as a Gaussian wave packet in  $Z$

$$b(Z) = [2\pi\xi^2]^{-1/4} \exp[-(Z-Z_0)^2/4\xi^2 + ik_{Z_0}Z_0], \quad (4)$$

times the product of a normalized plane wave function for the initial parallel translational motion and a spherical harmonic describing the initial molecular rotation. In Eq. (3),  $L_x = L_y (=a)$ , we will be dealing with a square lattice) are the magnitudes of the lattice vectors along  $X$  and  $Y$ ,  $\rho = (X, Y)$ , and  $\mathbf{K}_0$  is the vector of initial parallel momenta ( $k_{X_0}, k_{Y_0}$ ). In Eq. (4),  $\xi$  is the width of the wave packet which is centered on  $Z_0$  and travels in the negative  $Z$  direction with an average translational momentum  $k_{Z_0}$ .

In a wave packet calculation, the grid in the scattering coordinate can be made smaller if a separate grid which extends to larger values of  $Z$  is used to bring in the initial wave function.<sup>38</sup> In the separate grid, the same grid spacing is used, but the number of points used ( $N_{Z_{sp}}$ ) is larger. The separate grid is used to hold the diffractively and rotationally elastic channel until this channel can be accommodated on the range of the “regular” grid where the molecule-surface potential is significant and the absorbing potential (see below) is zero. Accommodation on the full grid is judged to be possible if the norm of the wave function that cannot be contained on this range of the regular grid is less than a tolerance parameter  $\text{tol}_{sp}$ . At the beginning two grids are used, but after the wave function is transferred to the regular grid propagation continues using one grid only. The separate grid method is used in both the CCWP method and the SAWP method, and was discussed in detail in Ref. 63.

Several different numerical algorithms are available to perform the time propagation of the wave function.<sup>64</sup> In the present work, we use the Chebyshev propagation method.<sup>83</sup> It involves the repeated evaluation of the action of the Hamiltonian on the wave function. The number of times that the action of the Hamiltonian on the wave function must be evaluated is related to the time step and the spectral range,  $W$ , of the Hamiltonian,<sup>64</sup> defined as

$$W = \lambda_{\max} - \lambda_{\min}, \quad (5)$$

where  $\lambda_{\max}$  and  $\lambda_{\min}$  are the maximum and minimum eigenvalues associated with the wave function. The computational cost of the wave packet propagation therefore depends sensitively on the spectral range associated with the wave packet method,<sup>59,64</sup> and the spectral range associated with the CCWP and SAWP methods is considered in some detail in Sec. II D.

The calculation of  $S$ -matrix elements involves the projection of the wave function on asymptotic diffraction-rotation eigenstates. We use a recent method devised by Balint-Kurti *et al.*,<sup>41,45,84</sup> in which the wave function is analyzed at a fixed value of the scattering coordinate ( $Z_\infty$ ), similar to what is done in the time-independent close-coupling (CC) method.<sup>66</sup> The wave function is projected on rotation-diffraction eigenstates at regular time intervals, obtaining time-dependent coefficients

$$C_{j'm'_jnm}(Z_\infty, t) = \sqrt{1/(L_x L_y)} \int_\rho \int_\Omega \Psi(Z_\infty, \rho, \theta, \phi, t) \times \exp[-i(\mathbf{K}_0 + \mathbf{G}_{nm})\rho] \times Y_{j'm'_j}^*(\theta, \phi) d\rho d\Omega. \quad (6)$$

In Eq. (6),  $n$  and  $m$  are the diffraction quantum numbers associated with the final translational state of the molecule, and  $\mathbf{G}_{nm}$  is the reciprocal lattice vector

$$\mathbf{G}_{nm} = \left( \frac{2\pi n}{L_x}, \frac{2\pi m}{L_y} \right). \quad (7)$$

Furthermore,  $j'$  and  $m'_j$  are the rotational quantum numbers associated with the molecule's final rotational state. The  $S$ -matrix elements  $S_{j'm'_jnmj_0m_{j_0}}(E)$  for a ( $j_0m_{j_0} \rightarrow j'm'_jnm$ ) transition are calculated from the  $C_{j'm'_jnm}(Z_\infty, t)$  using time to energy Fourier transforms.<sup>41,45,84</sup> The probabilities  $P(j_0m_{j_0} \rightarrow j'm'_jnm)$  are obtained from

$$P(j_0m_{j_0} \rightarrow j'm'_jnm) = |S_{j'm'_jnmj_0m_{j_0}}(E)|^2. \quad (8)$$

A nice feature of the asymptotic analysis method discussed above and also shared by some other methods<sup>60,61</sup> is that the scattered wave function is not needed beyond the analysis value of the scattering coordinate  $Z_\infty$ . Therefore, the grid in the scattering coordinate needs to contain only the range over which the potential acts plus a small interval which lies beyond  $Z_\infty$  and is used for absorbing the scattered wave packet. For this purpose, we add an optical potential of the quadratic form<sup>62</sup>

$$V_I(Z) = -iA_2 \left[ \frac{3}{2} \bar{Z}^2 \right], \quad (9a)$$

$$\bar{Z} = (Z - Z_I^{\min})/L, \quad (9b)$$

to the Hamiltonian of Eq. (1), the optical potential being defined over the range  $[Z_I^{\min}, Z_I^{\min} + L]$ .

## B. The close-coupling wave packet (CCWP) method

The CCWP method<sup>7-9,14</sup> is a hybrid wave packet method, meaning that a close-coupling representation is used for some, but not all, of the degrees of freedom other than the scattering coordinate. Using a close-coupling representation for the rotational degrees of freedom, but a DVR representation for the translational degrees of freedom, the wave function is written

$$\Psi(t) = \sum_{jm_j} \chi_{jm_j}^{j_0m_{j_0}}(\mathbf{R}, t) Y_{jm_j}(\theta, \phi). \quad (10)$$

In Eq. (10), the functions  $\chi_{jm_j}^{j_0m_{j_0}}(\mathbf{R}, t)$  represent the center-of-mass translational motion for the rotational states included in the expansion of the wave function. Along  $Z$ ,  $Y$ , and  $X$ ,  $N_z$ ,  $N_y$ , and  $N_x$  regularly spaced grid points are used. For a square lattice, a square grid of points in  $X$  and  $Y$  is used ( $N_y = N_x$ ). In the rotational expansion,  $N_{\text{rot}}$  rotational states

are included,  $j$  ranging from 0 to  $j_{\max}$ , and the magnetic rotational quantum number  $m_j$  ranging from  $-j$  to  $+j$  for each  $j$ .

Using the expansion of Eq. (10), the action of the kinetic energy operator associated with the translational motion of the molecule is evaluated efficiently<sup>85,86</sup> by transforming the translational functions to momentum space using consecutive FFT's (along  $Z$ ,  $Y$ , and  $X$ ) of the  $\chi_{jm_j}^{j_0 m_{j_0}}(\mathbf{R}, t)$ . The associated computational cost scales as  $N_z N_{xy} N_{\text{rot}} \times (\log N_z + \log N_y + \log N_x)$ , where  $N_{xy}$  is the product of  $N_y$  and  $N_x$ . The actual kinetic energy operation is performed together with the rotational energy operation in the combined momentum/angular momentum space by multiplying the value of the wave function at each grid point by the sum of the kinetic and rotational energies, which scales as  $N_z N_{xy} N_{\text{rot}}$ . This is followed by an inverse 3D Fourier transform back to coordinate space.

The potential energy operation is performed by premultiplying the vector  $\chi_{jm_j}^{j_0 m_{j_0}}(\mathbf{R}, t)$  with a potential coupling matrix on each point  $(Z, Y, X)$ . The elements of the matrix are

$$V_{j'm'_j m_j}(\mathbf{R}) = \int Y_{j'm'_j}^*(\theta, \phi) V(\mathbf{R}, \theta, \phi) Y_{jm_j}(\theta, \phi) d\Omega. \quad (11)$$

If no attention is paid to the possible sparseness of the matrix, the potential energy operation scales as  $N_z N_{xy} N_{\text{rot}}^2$ . If, on the other hand, the potential coupling matrix is sparse because many coupling terms are zero over the entire range of the scattering coordinate, the scaling is given by  $N_z N_{xy} N_{\text{rot}} N_{\text{coup}}^{\text{rot}}$ , where  $N_{\text{coup}}^{\text{rot}}$  is the average number of rotational states the potential couples to a given rotational state. This will be useful if, to describe the dependence of the molecule-surface potential on the molecular orientation, the potential is expanded in spherical harmonics  $Y_{j'' m''}$  and only low order (relative to the maximum value of  $j$  in the rotational basis set) expansion functions are used. In such a case, the matrix elements  $V_{j'm'_j m_j}(\mathbf{R})$  with widely differing  $j'$  and  $j$  and/or widely differing  $m'_j$  and  $m_j$  will be zero because the integrals  $\langle j'm'_j | j''m'' | jm_j \rangle$  are zero for all  $j''$  and  $m''$  contained in the potential expansion. This was true in the previous investigation<sup>63</sup> but not in the present work. Here, we will mostly consider whether advantage can be taken of the potential coupling matrix being sparser at larger values of the scattering coordinate, due to certain coupling matrix elements being important only at short range (close to the surface).

The method we developed to reduce both the CPU time and storage requirements associated with the potential energy operation basically involves not using coupling matrix elements in the multiplication once their absolute values become less than some threshold value  $V_t$  at larger values of the scattering coordinate. The method used is very simple: For each coupling matrix element [Eq. (11)] and each grid value of  $X$  and  $Y$ , the size of a particular matrix element is scanned as a function of  $Z$ , moving from the largest value of the scattering coordinate on the grid inwards. An array is used to keep track of the value of  $Z$  at which the matrix element exceeds the threshold value for at least one grid

point  $(X, Y)$ , say at  $Z_p$ . In the propagation, the multiplication with the potential coupling matrix element is then only performed for grid values of  $Z \leq Z_p$ . Using the same maximum value  $Z_p$  for all grid points  $(X, Y)$  allows efficient vectorization over  $X$  and  $Y$  simultaneously, which is quite important if the calculations are performed on a vector processing computer like the one used in the present work (a Cray C98). In such a case, gains made by achieving smaller vector lengths may be rather insignificant in case the number of vectors remains the same.

If the sparseness of the potential at intermediate and long range is taken into account in the manner described above, the scaling of the potential energy operation with the number of rotational states will be no longer clear (it will depend on the range of the coupling terms). In Sec. III, we will give results concerning the resulting improvement in efficiency for the model problem under investigation in the present work.

In addition to the action of the Hamiltonian on the wave function, the propagation of the wave function in time also involves operations which are intrinsic to the propagation algorithm used. The Chebyshev algorithm involves additions and multiplications with phase factors which all scale as  $N_z N_{xy} N_{\text{rot}}$ .

The calculation of the initial wave function [Eqs. (3) and (4)] can be performed trivially by calculating  $b(Z) \times \exp[i\mathbf{K}_0 \rho]$  on the grid in  $X$ ,  $Y$ , and  $Z$ . Arbitrary angles of incidence can be handled by extending the FFT scheme using the shifting theorem of Fourier analysis, as described in Ref. 54. The extra (shifting) operations required scale as  $N_z N_{xy} N_{\text{rot}}$ . In the calculation of the  $S$ -matrix elements, the projection of the wave function on the rotation-diffraction eigenstates is done using consecutive FFT's of  $\chi_{jm_j}^{j_0 m_{j_0}}(Z_\infty, Y, X, t)$  along  $Y$  and  $X$  for all rotational states present in the basis set [see Eq. (6)].

The amount of central memory required when using the Chebyshev algorithm to propagate the wave function is four storage arrays,<sup>87</sup> where the memory taken up by one storage array is the amount of memory required to hold the full wave function. In the CCWP method, the memory required to store the wave function is  $2 \times N_z N_{xy} N_{\text{rot}}$  (the factor 2 is from the wave function being complex). If the potential coupling matrix is full and no use is made of coupling matrix elements being of short range, the amount of memory required to store the matrix on the grid is  $N_z N_{xy} N_{\text{rot}} (N_{\text{rot}} + 1)$  (the coupling matrix being complex-Hermitian, and storing only the upper triangle). If use is made of certain coupling matrix elements being important only at short range, the amount of central memory required to hold the coupling matrix will depend on just how sparse the coupling matrix is at longer range. The improvements we achieved in the present case are discussed in Sec. III.

### C. The symmetry adapted rotationally and diffractively close-coupled wave packet (SAWP) method

It is also possible to use a full close-coupling representation for all the degrees of freedom other than the scattering coordinate

$$\Psi(t) = \sum_{jm_jnm} f_{jm_jnm}^{j_0m_{j_0}}(Z,t) \phi_{nmjm_j}(X,Y,\theta,\phi), \quad (12a)$$

where

$$\begin{aligned} \phi_{nmjm_j}(X,Y,\theta,\phi) = & \sqrt{1/A} \exp[i(\mathbf{K}_0 + \mathbf{G}_{nm})\rho] \\ & \times Y_{jm_j}(\theta,\phi). \end{aligned} \quad (12b)$$

In Eq. (12b),  $A$  is the surface area of the surface unit cell. We have called the resulting method the rotationally and diffractively close-coupled wave packet (RDWP) method.<sup>63</sup>

An advantage of using a close-coupling representation also for the diffractive degrees of freedom is that the kinetic energy operation can be done more efficiently. Because the wave function is expanded in translational eigenfunctions for the  $X$  and  $Y$  degrees of freedom, Fast Fourier transforms (FFT's) need to be carried out for  $Z$  only. However, this advantage will often be more than offset by the increased cost of the potential energy operation.

The potential energy operation is expected to be more expensive in the RDWP method because, for a full potential coupling matrix, the potential energy operation will now scale with  $N_z N_{\text{dif}}^2 N_{\text{rot}}^2$ , which is much more unfavorable than the CCWP scaling ( $N_z N_{xy} N_{\text{rot}}^2$ ,  $N_{xy}$  will be approximately equal to  $N_{\text{dif}}$ , which is the number of diffraction states included in the basis set). The problem may be somewhat alleviated if, in the potential expansion, only diffraction expansion functions of low order are required, and only rotational expansion functions with low  $j$  are required. In this case the scaling may be given as  $N_z N_{\text{coupl}}^{\text{dif}} N_{\text{dif}} N_{\text{coupl}}^{\text{rot}} N_{\text{rot}}$ , where  $N_{\text{coupl}}^{\text{dif}}$  is the average number of diffraction states a given diffraction state will be coupled to by the potential, and  $N_{\text{coupl}}^{\text{rot}}$  has previously been defined in Sec. II B. Upper bounds to  $N_{\text{coupl}}^{\text{dif}}$  are 5 and 13 for a diffraction order  $O_p$  of 1 and 2 in the potential expansion respectively ( $O_p = |n| + |m|$ ), and  $N_{\text{coupl}}^{\text{dif}} = 9$  and 25 for  $n_{\text{max}}^p$  is 1 and 2, respectively, where  $|m| \leq |n| \leq n_{\text{max}}^p$ . However, apart from exceptional cases<sup>63</sup> the RDWP method is not expected to be more efficient than the CCWP method, the potential energy operation being more expensive by a factor  $N_{\text{dif}}/N_{xy} N_{\text{coupl}}^{\text{dif}}$ .

A different situation may arise in case the symmetry of the lattice is used. For the case of a diatomic molecule interacting with a rigid lattice surface of a given point group symmetry, the molecule-surface potential may be expanded in symmetry adapted functions. If the diatomic is homonuclear, these functions should be symmetric with respect to exchanging the atoms of the molecule and transform according to the totally symmetric representation of the point group associated with the crystal face (the  $A_1$  representation of the  $C_{4v}$  group for the case of the square lattice that we consider)

$$\begin{aligned} V(Z,\rho,\theta,\phi) = & \sum_{\Gamma, j m_j \Gamma_d n m} c_{A_1 \Gamma, j m_j \Gamma_d n m}(Z) \\ & \times v_{A_1 \Gamma, j m_j \Gamma_d n m}(\rho,\theta,\phi). \end{aligned} \quad (13)$$

In Eq. (13), due to the inversion symmetry of the molecule  $j$  takes on even values only. In the symmetry adapted close-

TABLE I. The  $D_{ij}^{(E)}(B^{-1})$  matrices used in this work are given for the operation  $B$  belonging to the  $C_{4v}$  group. The  $C_4$  operation rotates the positive  $x$  axis on to the positive  $y$  axis, and  $\sigma_{d1}$  is along the line  $x=y$ .

$B$	$E$	$C_4$	$C_4^2$	$C_4^3$	$\sigma_{xz}$	$\sigma_{yz}$	$\sigma_{d1}$	$\sigma_{d2}$
$D_{11}^{(E)}(B^{-1})$	1	0	-1	0	1	-1	0	0
$D_{12}^{(E)}(B^{-1})$	0	1	0	-1	0	0	1	-1
$D_{21}^{(E)}(B^{-1})$	0	-1	0	1	0	0	1	-1
$D_{22}^{(E)}(B^{-1})$	1	0	-1	0	-1	1	0	0

coupling wave packet (SAWP) method, we then expand the wave function in symmetry adapted rotation-diffraction functions as

$$\begin{aligned} \Psi(t) = & \sum_{\Gamma \alpha \Gamma_r j m_j \Gamma_d n m} f_{\Gamma \alpha \Gamma_r j m_j \Gamma_d n m}^{j_0 m_{j_0}}(Z,t) \\ & \times g_{\Gamma \alpha \Gamma_r j m_j \Gamma_d n m}(\rho,\theta,\phi) \exp[i\mathbf{K}_0 \rho]. \end{aligned} \quad (14)$$

As can be seen from Eq. (14), a grid representation is used in  $Z$ , using  $N_z$  equally spaced points. In Eqs. (13) and (14),  $m_j$  takes on only positive values. The symbol  $\Gamma$  denotes the irreducible representation  $\Gamma$  of a symmetrized rotation-diffraction function and  $\alpha$  its subspecies,  $\Gamma_r$  the irreducible representation of the symmetry adapted rotational function(s) and  $\Gamma_d$  the irreducible representation of the symmetrized diffraction function(s), which are combined to obtain a rotation-diffraction function belonging to the subspecies  $\alpha$  of the irreducible representation  $\Gamma$ . As will be explained in some detail below, the indexes making up the subscripts define the symmetry-adapted rotation-diffraction functions of Eqs. (13) and (14) in an unambiguous manner.

We will now first consider the construction of a basis set of symmetrized rotation-diffraction eigenstates. We start by constructing symmetry-adapted diffraction functions. This is done by operating on  $\exp(i(\mathbf{G}_{nm}\rho))$  ( $n \geq m \geq 0$ ) with the group projection operator<sup>88</sup>

$$O_{ij}^{(\Gamma)} = \frac{n_{\Gamma}}{0G} \sum_{B \in G} D_{ij}^{(\Gamma)}(B^{-1}) B. \quad (15)$$

In Eq. (15),  $\Gamma$  is the irreducible representation that is projected out,  $0G$  is the order of the group (8 for  $C_{4v}$ ),  $n_{\Gamma}$  is the dimension of the irreducible representation  $\Gamma$  (2 for  $E$  and 1 for the other irreducible representations),  $B$  is an operation belonging to the group, and  $D_{ij}^{(\Gamma)}(B^{-1})$  is an  $n_{\Gamma}$  by  $n_{\Gamma}$  irreducible matrix representation of the inverse operation. For the one-dimensional irreducible representations,  $D_{ij}^{(\Gamma)}(B^{-1})$  is simply equal to the character  $[\chi^{(\Gamma)}(B)]^{-1}$  corresponding to the operation  $B$ . For the  $E$  irreducible representation of the  $C_{4v}$  group, the  $D$  matrices are given in Table I.

By operating with the group projection operator on  $\exp[i(\mathbf{G}_{nm}\rho)]$  with  $n \geq m \geq 0$ , linear combinations of degenerate diffraction eigenfunctions are formed, where the diffraction functions transform among one another under the operations of the point group and form what we term a "diffraction manifold" which is characterized by the values of  $n \geq m \geq 0$ . The linear combinations formed belong to different subspaces  $\Delta_i^{(\Gamma)}$ , each corresponding to a subspecies of the various irreducible representations. For the  $C_{4v}$  group, the

symmetries are  $A_1$ ,  $A_2$ ,  $B_1$ ,  $B_2$ ,  $E^1$ , and  $E^2$ , where we use superscripts to distinguish the two subspecies of  $E$  symmetry. Furthermore, for one and the same value of the index  $j$  the projection operators  $O_{ij}^{(E)}$  ( $i=1,2$ ) obtained using the  $D$  matrices of Table I generate functions of  $E^1$  and  $E^2$  symmetry which are partners. This will be relevant when the symmetry adapted diffraction functions are combined with symmetry adapted rotational functions to form symmetry adapted rotation-diffraction functions of  $A_1$  symmetry.

Application of the group projection operator of Eq. (15) yields  $1A_1$  function for  $n=m=0$ ,  $1A_1$ ,  $1B_1$ ,  $1E^1$ , and  $1E^2$  function for diffraction manifolds with  $n>m=0$ ,  $1A_1$ ,  $1B_2$ ,  $1E^1$ , and  $1E^2$  function for diffraction manifolds with  $n=m>0$ , and  $1A_1$ ,  $1A_2$ ,  $1B_1$ ,  $1B_2$ ,  $2E^1$ , and  $2E^2$  functions for diffraction manifolds with  $n>m>0$ . The derivation of expressions for the symmetry adapted functions is straightforward, and we only give the expressions for the  $E$  functions for diffraction manifolds with  $n>m>0$

$$H_{E^1nm}(\rho) = 2\sqrt{1/A} \sin k_n x \cos k_m y, \quad (16a)$$

$$H_{E^2nm}(\rho) = 2\sqrt{1/A} \sin k_n y \cos k_m x, \quad (16b)$$

$$H_{E^1mn}(\rho) = 2\sqrt{1/A} \sin k_m x \cos k_n y, \quad (16c)$$

$$H_{E^2mn}(\rho) = 2\sqrt{1/A} \sin k_m y \cos k_n x. \quad (16d)$$

In Eq. (16),  $k_n = n \times 2\pi/a$ . Furthermore, Eqs. (16a) and (16b) define partners, and similarly so for Eqs. (16c) and (16d).

Symmetry adapted rotation functions can be constructed by operating with the group projection operator [Eq. (15)] on the spherical harmonics  $Y_{jm_j}(\theta, \phi)$ , where spherical harmonics characterized by the same  $j$  value and the same absolute value of  $m_j$  are said to form a "rotational manifold." For the  $C_{4v}$  group, application of the group projection operator yields  $1A_1$  function for  $m_j=0$ ,  $1E^1$ , and  $1E^2$  function for  $|m_j|=1, 3, 5, 7, \dots$ ,  $1B_1$  and  $1B_2$  function for  $|m_j|=2, 6, 10, \dots$ , and  $1A_1$  and  $1A_2$  function for  $|m_j|=4, 8, 12, \dots$ . For instance, we have

$$R_{A_1j|m_j|}(\theta, \phi) = \sqrt{\frac{1}{2}} \{Y_{j|m_j|}(\theta, \phi) + Y_{j-|m_j|}(\theta, \phi)\}, \quad (17a)$$

$$R_{A_2j|m_j|}(\theta, \phi) = \frac{1}{i} \sqrt{\frac{1}{2}} \{Y_{j|m_j|}(\theta, \phi) - Y_{j-|m_j|}(\theta, \phi)\}, \quad (17b)$$

$|m_j|=4, 8, 12, \dots$

A symmetry adapted basis set containing rotation-diffraction basis functions of the totally symmetric representation can now be obtained by combining diffraction functions belonging to the same diffraction manifold and rotation functions belonging to the same rotational manifold observing the direct product rules which are appropriate for the point group under consideration. For the  $C_{4v}$  group, the only nontrivial relation for functions which are totally symmetric involves  $E$  functions and can be written<sup>89</sup>

$$A_1(\rho, \theta, \phi) = \sqrt{\frac{1}{2}} \{E^1(\rho) \otimes E^1(\theta, \phi) + E^2(\rho) \otimes E^2(\theta, \phi)\}. \quad (18)$$

In Eq. (18), the functions  $E^1(\rho)$  and  $E^2(\rho)$  are partners, and the same is true for  $E^1(\theta, \phi)$  and  $E^2(\theta, \phi)$ . For instance, the two  $A_1$  basis functions that can be obtained from the ( $n=2$ ,  $m=1$ ) diffraction manifold and a  $|m_j|=1$  rotational manifold are given by

$$g_{A_1Ej1E21}(\rho, \theta, \phi) = \sqrt{\frac{1}{2}} \{H_{E^121}(\rho)R_{E^1j1}(\theta, \phi) + H_{E^221}(\rho)R_{E^2j1}(\theta, \phi)\}, \quad (19a)$$

$$g_{A_1Ej1E12}(\rho, \theta, \phi) = \sqrt{\frac{1}{2}} \{H_{E^112}(\rho)R_{E^1j1}(\theta, \phi) + H_{E^212}(\rho)R_{E^2j1}(\theta, \phi)\}. \quad (19b)$$

Equations (19a) and (19b) illustrate the meaning of the subscripts of the symmetry adapted functions  $v$  and  $g$  in Eqs. (13) and (14) respectively, and show how the indices in the subscripts define these functions unambiguously for the  $C_{4v}$  group. The first index denotes the symmetry of the rotation-diffraction function, the second index the irreducible representation to which the rotational functions contained in the rotation-diffraction function belong, the third index is the rotational quantum number  $j$  and the fourth index is the absolute value of the magnetic rotational quantum number  $|m_j|$ , meaning that rotational functions with  $m_j = +|m_j|$  and  $m_j = -|m_j|$  are mixed in. The fifth index  $\Gamma_d$  denotes the irreducible representation to which the diffraction functions contained in the rotation-diffraction function belong, and the sixth and seventh indices are  $n$  and  $m$ , respectively, which define the diffractive manifold to which the diffraction function belongs. The symmetry adapted rotation-diffraction functions  $g_{A_1\Gamma_djm_j\Gamma_dnm}(\rho, \theta, \phi)$  and  $v_{A_1\Gamma_djm_j\Gamma_dnm}(\rho, \theta, \phi)$  are defined without ambiguity through the direct product rules [like Eq. (18)] and the procedure (outlined above) by which symmetry adapted diffraction functions and symmetry adapted rotation functions are obtained. Note in particular how our notation distinguishes between  $g_{A_1\Gamma_djm_jEnm}(\rho, \theta, \phi)$  and  $g_{A_1\Gamma_djm_jEmn}(\rho, \theta, \phi)$ , where  $n>m$  in both cases [see Eqs. (16a)–(16d)].

Now that we have outlined how a symmetry-adapted basis can be constructed, we will consider the potential energy operation in the SAWP method. In the SAWP method, the evaluation of the potential energy operation involves premultiplying the vector  $f_{\Gamma\alpha\Gamma_djm_j\Gamma_dnm}^{j_0m_{j_0}}(Z, t)$  with the potential coupling matrix at each grid point in  $Z$ . The elements of this matrix are

$$V_{\Gamma'\alpha'\Gamma'_djm'_j\Gamma'_dnm'\Gamma\alpha\Gamma_djm_j\Gamma_dnm}(Z) = \int g_{\Gamma'\alpha'\Gamma'_djm'_j\Gamma'_dnm'}(\rho, \theta, \phi) V(\mathbf{R}, \theta, \phi) \times g_{\Gamma\alpha\Gamma_djm_j\Gamma_dnm}(\rho, \theta, \phi) d\rho d\Omega$$

$\Gamma' = \Gamma \quad \text{and} \quad \alpha' = \alpha,$  (20a)



$$V_{\Gamma'\alpha'\Gamma'_j m'_j \Gamma'_d n'_m \Gamma \alpha \Gamma_j m_j \Gamma_d n m}(Z) = 0 \quad \text{otherwise.} \quad (20b)$$

Expanding the wave function as in Eq. (14) thus has the advantage that the potential coupling matrix becomes block diagonal, making the potential energy operation less expensive. Apart from the term  $\exp[i\mathbf{K}_0\rho]$ , the initial rotation-diffraction function will contain only one irreducible representation (for  $|m_j|=0$  or odd) or two irreducible representations (for  $|m_j|>0$  and even, from now on we consider the case of a homonuclear diatomic interacting with a square lattice). However, for an arbitrary angle of incidence, this will not help one to reduce the number of rotation-diffraction functions required in the basis set: The presence of the term  $\exp[i\mathbf{K}_0\rho]$  leads to off-diagonal couplings in the kinetic energy operation. While the kinetic energy matrix is no longer diagonal in this case, it is still highly blocked, because the couplings are only between between symmetry adapted states belonging to the same diffraction manifold.

However, it is possible to reduce the number of rotation-diffraction basis functions in the case of normal incidence<sup>65</sup>: In such a case rotation-diffraction functions of no more than two irreducible representations need to be included in the basis set. In the special case we consider (the initial value of  $m_j$  is zero) only symmetrized rotation-diffraction functions belonging to the  $A_1$  representation need to be included. Because these functions are eigenfunctions of the rotation-diffraction part of the Hamiltonian, the SAWP method shares with the RDWP method the advantage that, for performing the kinetic energy operation, FFT's need to be carried out for the  $Z$  degree of freedom only. In the SAWP method, the (translational+rotational) kinetic energy operation scales as  $N_Z \log(N_Z)N_{A_1}$ , where  $N_{A_1}$  is the number of symmetrized rotation-diffraction states included in the basis set and belonging to the  $A_1$  irreducible representation (typically, for  $C_{4v}$  symmetry of the lattice  $N_{A_1} = \frac{1}{8}N_{\text{dif}}N_{\text{rot}}$ ). The kinetic energy operation is thus much cheaper in the SAWP method than in the CCWP method both because the FFT's along  $X$  and  $Y$  can be avoided and because  $N_{A_1}$  is much less than  $N_{xy}N_{\text{rot}}$  (by approximately a factor 8).

Of course, the SAWP method will be more efficient than the CCWP method only if the gains made by performing the kinetic energy operation more efficiently are not offset by losses incurred in performing the potential energy operation less efficiently. For normal incidence,  $m_{j_0}=0$ , and a full potential coupling matrix, the potential energy operation will scale as  $N_Z N_{A_1}^2$ , which means that a huge saving is obtained at least relative to the RDWP method. Additional savings can be obtained if the expansion of the potential [Eq. (13)] can be limited to terms that are of low order in diffraction and rotation, such that many coupling matrix elements are zero over the entire range of the scattering coordinate. If the potential energy operations in the RDWP method are more expensive than those in the CCWP method by a factor  $N_{\text{dif}}/N_{xy}N_{\text{coupl}}^{\text{dif}}$ , this scale factor changes to approximately  $\frac{1}{2}N_{A_1}/N \times N_{\text{dif}}/N_{xy}N_{\text{coupl}}^{\text{dif}}$  for the SAWP method ( $N=N_{\text{dif}}N_{\text{rot}}$ , and the factor  $\frac{1}{2}$  comes from the coupling matrix being real symmetric in the SAWP method rather than complex Hermitian, as in the CCWP and RDWP methods if

the potential depends on  $\phi$ ). In Sec. III, we will discuss to what extent it is possible to limit the expansion of the potential to low order terms for the fairly corrugated model system under investigation, and whether the SAWP method is then less expensive computationally than the CCWP method.

In performing the potential energy operation, extra savings may also be obtained if many potential matrix coupling elements are important only at short range. The method adopted is principally similar to the one used in the CCWP method. For each coupling matrix element [Eq. (20)], the size of the element is scanned as a function of  $Z$ , moving from the largest value of the scattering coordinate on the grid inwards. Let us suppose that the absolute value of the coupling matrix elements becomes larger than  $V_i$  at  $Z_p$ . For the particular matrix element, the multiplication is then carried out for values of  $Z$  smaller than or equal to  $Z_p$  only.

To take full advantage of the increased sparseness of the potential coupling matrix at longer range on a vector computer, in the SAWP method a strategy has to be adopted which is somewhat more complicated than the one used in the CCWP method. Vectorizing over the  $Z$  degree of freedom for all matrix coupling elements will not be very efficient. This strategy only has the effect of decreasing the average vector length, while the number of vectors is not decreased. Vectorizing over the states included in the basis set is of course not efficient at long range, where a given state will only couple to a few others.

We found that the most efficient scheme consists of a combination. For elements which are important over a long range of the scattering coordinate (longer than say  $\Delta Z_r$ ), the multiplication is vectorized over  $Z$ . The multiplications which remain to be performed at short range are done vectorizing over states, skipping zero-matrix elements and the coupling matrix elements already handled in the part vectorized over  $Z$ . Of course, the scheme will be optimal only for one particular value for  $\Delta Z_r$ . The optimal range is estimated by calculating, for each conceivable range  $\Delta Z$ , the number of vectors  $N_{v_z}(\Delta Z)$  which can be made over  $Z$  as well as their average length  $l_{v_z}(\Delta Z)$ , and also the number of vectors over states  $N_{v_s}(\Delta Z)$  as well as the associated average vector lengths  $l_{v_s}(\Delta Z)$ . The optimal range  $\Delta Z_r$  is then calculated as

$$\Delta Z_r = \min(\Delta Z) \{ N_{v_z}(\Delta Z)(t_z^s + l_{v_z}(\Delta Z)t_z^i) + N_{v_s}(\Delta Z)(t_s^s + l_{v_s}(\Delta Z)t_s^i), \quad (21)$$

where  $t_z^s$  and  $t_s^s$  are start-up CPU times for multiplications vectorizing over  $Z$  and states respectively, and  $t_z^i$  and  $t_s^i$  are incremental CPU times. The values of  $t_z^s$  and  $t_s^s$  and of  $t_z^i$  and  $t_s^i$  will depend on the computer used, and were obtained from test calculations in the present work.

In the SAWP method, the propagation of the wave function (the Chebyshev algorithm) scales as  $N_z N_{A_1}$ , compared to  $N_z N_{xy} N_{\text{rot}}$  for the CCWP method. Because  $N_{A_1}$  should be approximately  $\frac{1}{8}N_{xy}N_{\text{rot}}$ , the propagation algorithm should require much less CPU time in the CCWP method.

We now turn our attention to the setting up of the initial wave function and the asymptotic analysis. In the SAWP method, the calculation of the initial wave function [Eqs. (3) and (4)] simply involves setting  $f_{A_1 j_0 A_1 00}^{j_0 0}(Z, t=0)$  equal to

$b(Z)$ , while setting all other expansion coefficients to zero. The asymptotic analysis is performed by first calculating time-dependent coefficients  $C_{A_1 j m_j \Gamma_{d n m}}(Z_\infty, t)$ ; these are simply equal to  $f_{A_1 \Gamma_{r j m_j \Gamma_{d n m}}}^{j_0 m_{j_0}}(Z_\infty, t)$ . From these coefficients,  $S'$ -matrix elements labeled by the same indices are calculated. Defining the transformation

$$g_\mu = \sum_i \phi_i T_{i\mu}, \quad (22a)$$

where  $\mu$  and  $i$  are collective indexes and the symmetry adapted and nonadapted functions  $g$  and  $\phi$  are defined in Eqs. (12) and (14), respectively, the actual  $S$  matrix for rotation-diffraction transitions [Eq. (8)] can be obtained by applying the transformation

$$S = T S' T^\dagger. \quad (22b)$$

The expressions for  $S$  in terms of  $S'$  along with the symmetry restrictions this places on  $S$ -matrix elements and probabilities can be obtained from some tedious, but otherwise straightforward algebra. Note that  $T$  defines a direct transformation of the basis rather than a transformation of the matrix representation of the wave function.<sup>90</sup>

One advantage of the SAWP method over the CCWP method is that there is an enhanced freedom in the choice of diffraction eigenstates to expand in. The spectral diffraction basis effectively used in the CCWP method is a square grid of  $N_{xy}$  points in the two-dimensional  $(p_x, p_y)$  momentum space. In case a close-coupling representation is used for the diffractive degrees of freedom, it is also possible to use a diamond-shaped grid in momentum space, by including only diffraction states up to diffraction order  $M_{\text{dif}}$ , where the diffraction order  $O_w = |n| + |m|$ , in constructing the symmetry adapted basis. The number of states required for convergence in such a diamond-shaped grid may well be less than the number required for convergence using a square grid. This is investigated in Sec. III.

Another advantage gained from using the full expansion in molecular eigenstates in the SAWP method is that, if the collision energy distribution is not too broad, the energy of the motion away from the surface will be reasonably well defined for each scattered channel. This means that the procedure used to absorb the scattered wave function can be optimized by making the optical potential channel dependent. In all cases we use a fixed value for  $L$ , the range over which the optical potential acts, which enables us to work with a grid of fixed size. However, the proportionality constant of the optical potential [ $A_2$  for a quadratic potential, see Eq. (9a)] is adjusted to the translational energy with which the scattered channel is expected to emerge, using procedures described in Ref. 62, to obtain optimal absorption (see also Sec. II F).

In the SAWP method, the amount of memory required to store the wave function is  $2 \times N_z N_{A_1}$ , which is much less than in the CCWP method. In case the potential coupling matrix is full, the amount of memory required to store its upper triangle is  $\frac{1}{2} N_z N_{A_1} (N_{A_1} + 1)$  (as was mentioned before, the potential coupling matrix is real symmetric in the SAWP method). The amount of memory required to hold the

potential in case use is made of the sparseness of the potential coupling matrix will depend on the particular scattering problem. Results for the model problem investigated in this work are given in Sec. III.

## D. The spectral range associated with the different methods

For any wave packet method, the number of Hamiltonian operations required to propagate the wave function over some given time  $\Delta t$  is linearly proportional to the spectral range of the Hamiltonian.<sup>8,59,64</sup> For the methods discussed in the previous subsections, the spectral range follows from using

$$\lambda_{\text{max}} = T_{\text{max}}^z + T_{\text{max}}^y + T_{\text{max}}^x + T_{\text{max}}^{\text{rot}} + V_{\text{max}}, \quad (23a)$$

$$\lambda_{\text{max}} = V_{\text{min}}, \quad (23b)$$

in Eq. (5). In Eq. (23a), the calculation of the maximum kinetic energies in  $Z$ ,  $Y$ , and  $X$  ( $T_{\text{max}}^z$ ,  $T_{\text{max}}^y$ , and  $T_{\text{max}}^x$ ) and of the maximum rotational energy  $T_{\text{max}}^{\text{rot}}$  is easily performed for both the CCWP and SAWP method, following either from the grid spacing employed for a particular degree of freedom or the parameters characterising the close-coupling expansion (like  $j_{\text{max}}$ ). In Eqs. (23),  $V_{\text{min}}$  is the minimum molecule-surface potential energy, which is usually known from the molecule-surface potential well depth. However, as discussed below the calculation of the maximum potential energy  $V_{\text{max}}$  is not so straightforward in the CCWP and SAWP methods.

It is a long standing practice to impose a maximum  $V_{\text{cut}}$  on the potential energy in order to reduce the spectral range. It is likewise useful to impose a maximum on the total kinetic energy.<sup>91</sup> Imposing a maximum  $T_{\text{cut}}$  on the total kinetic energy is easy in both the CCWP and SAWP methods, because in both methods the wave function can be obtained in the combined momentum/angular momentum representation. In the fully spectral representation the total kinetic energy operation simply becomes a multiplication to be carried out on each grid point in momentum space. Imposing the cut-off value  $T_{\text{cut}}$  is done simply by setting  $T$  equal to  $T_{\text{cut}}$  at any point for which  $T$  is larger than  $T_{\text{cut}}$ . In the CCWP and SAWP methods, the same value can be used for  $T_{\text{cut}}$ .

A great advantage of a method in which the potential energy operation is performed in the coordinate representation (FBR methods like the FBWP method<sup>58,59</sup>) is that a maximum  $V_{\text{cut}}$  can be imposed on the potential energy operator in the same manner, by simply putting  $V$  equal to  $V_{\text{cut}}$  at any point in coordinate space for which  $V$  is larger than  $V_{\text{cut}}$ . This advantage is not shared by methods employing the close-coupling representation or VBR. What one can do, however, is to impose a maximum  $V_{\text{max}}^{\text{cut}}$  on the orientationally averaged potential (in the CCWP method) or on the potential that is averaged both over the orientation of the molecule and over the projection of its position on the surface unit cell (in the SAWP method). Suppose that in the CCWP method, we expand the potential as

$$V(Z, Y, X, \theta, \phi) = \sum_{j \geq 0} C_j(Z, Y, X) V_j(\theta, \phi) \quad (24)$$

and in the SAWP method, we expand the potential as

$$V(Z, Y, X, \theta, \phi) = \sum_{j \geq 0} C_j(Z) V_j(X, Y, \theta, \phi). \quad (25)$$

Suppose that the expansion functions used in Eqs. (24) and (25) are normalized in such a way that their maximum absolute value is 1. In either case,  $V_0$  will be  $\sqrt{2\pi}Y_{00}$ . A maximum can then be imposed on the potential by, before calculating the potential coupling matrix, imposing a cut off on the potential energy expansion rather than the potential energy itself. This is done by setting, in all cases where we find that  $C_0 > V_{\max}^{\text{cut}}$ ,

$$C_0 = V_{\max}^{\text{cut}}, \quad (26a)$$

$$C_j = 0, \quad j \geq 1. \quad (26b)$$

The value of  $V_{\max}^{\text{cut}}$  that will be needed to get converged results will typically be somewhat higher than the cut-off value  $V_{\text{cut}}$  one would use if the potential energy operation were performed in the coordinate representation. To see this, suppose for a moment that we would use such a method, and that a cut-off value  $V_{\text{cut}}$  would be needed to get converged results. Now suppose we are using the CCWP method, and that for some point  $(X, Y, Z)$  the potential is lower than  $V_{\text{cut}}$  for a few orientations, but higher for most orientations. This will mean that the orientationally averaged potential is higher than  $V_{\text{cut}}$ . If we now impose a maximum on  $V$  by putting  $V_{\max}^{\text{cut}}$  equal to  $V_{\text{cut}}$  we are now in effect increasing the potential at points where  $V$  is low enough to affect our final results. Therefore, the value of  $V_{\max}^{\text{cut}}$  should be larger than  $V_{\text{cut}}$  and large enough to ensure that the potential is only modified at points  $(X, Y, Z)$  for which the potential is larger than  $V_{\text{cut}}$  for all orientations. Using a similar line of reasoning, it can be demonstrated that, in calculating the spectral range using

$$\lambda_{\max} = T_{\text{cut}} + c V_{\max}^{\text{cut}}, \quad (27)$$

it will be necessary to use a value of  $c$  larger than one, because the averaged potential will always be less than the maximum value of  $V$ . The spectral range associated with the close-coupling methods is thus larger than the spectral range associated with an FBR method (where  $\lambda_{\max} = T_{\text{cut}} + V_{\text{cut}}$ ). As a consequence, a disadvantage of the close-coupling methods is that, for a given timestep, a larger number of Hamiltonian operations are required for propagating the wave function in time in a stable manner.

In the calculations discussed in Sec. III,  $V_{\max}^{\text{cut}}$  is a parameter with respect to which convergence is sought. The value of  $c$  required by the CCWP and SAWP methods is established by trial and error. Selecting too small a value for  $c$  results in using a timestep that is too large and, consequently, instability in the propagation of the wave function, which usually shows up after taking only a few time steps. The difficulty with imposing a maximum on the potential when using a close-coupling representation is a larger disadvantage in the SAWP method than in the CCWP method because the close-coupling representation is used for two additional degrees of freedom in the SAWP method. As a result, the SAWP method is expected to require more Hamiltonian op-

erations per timestep (or smaller timesteps in case the same number of Hamiltonian operations per timestep is used).

## E. Model potential

The model potential we use here has recently been devised and used by us in calculations on scattering of  $\text{H}_2$  from  $\text{LiF}(001)$  at a collision energy of 0.1 eV.<sup>69,70</sup> For a full description of the model potential, the reader is referred to Ref. 70. Here, we only briefly review its most essential features, which ensure that the model potential is both a useful and realistic test example for comparing the performance of the SAWP and CCWP methods for an  $\text{H}_2$ -surface system of fairly high corrugation.

Essential components contained in the potential are (i) a long-ranged ( $\sim Z^{-3}$ ) attractive interaction, the anisotropy of which is described by the  $Y_{20}$  spherical harmonic, (ii) a medium-ranged electrostatic (quadrupole-ionic lattice<sup>92</sup>) interaction which contributes both to the anisotropy and the corrugation, favoring different orientations across the unit cell, and (iii) a short-ranged repulsive interaction, which leads to higher order corrugation terms and anisotropic terms which become increasingly important close to the surface. The last feature of the model potential makes it a useful test model for algorithms which try to exploit the increasing sparseness of the potential coupling matrix at longer range (Secs. II B and II C). The inclusion of the electrostatic interaction leads to a fairly large difference in the spectral ranges associated with the CCWP and SAWP methods (Sec. II D). No such large difference is observed when using the previously investigated<sup>63</sup> Wolken potential,<sup>66</sup> the corrugation of which is described by only a single Fourier term, while only the  $Y_{20}$  spherical harmonic is used to describe the anisotropy. The Wolken potential favors one orientation of the molecule across the unit cell.

For the CCWP calculations, the model potential<sup>70</sup> was first calculated for a number of molecular orientations for values of  $X$ ,  $Y$ , and  $Z$  corresponding to the grid points. Subsequently, the potential was expanded in spherical harmonics including functions with  $j_{\max}$  up to 6 (a total of 28 rotational functions). In the SAWP calculations we use the expansion of Eq. (13), retaining terms with diffraction order  $|n| + |m|$  up to 6 and  $j_{\max}$  up to 6. The expansion coefficients for the symmetry adapted rotation-diffraction functions were calculated from spherical harmonic coefficients obtained previously in a calculation employing 16 grid points along  $X$  and 16 points along  $Y$ . In both cases, convergence of the expansion with respect to the number of functions included was checked for by recalculating the potential from the expansion and comparing with the original model potential on a grid of points.

## F. Numerical details

The numerical values of the input parameters common to the CCWP and SAWP calculations presented here are given in Table II. Most of these parameters have already been discussed in Secs. II A–II D. The average initial momentum

TABLE II. Numerical parameters used as input in the calculations are given.

Parameter	CCWP	SAWP
Initial wave packet		
Width $\xi$ (bohr)	1.118	1.118
Initial position $Z_0$ (bohr)	25.0	25.0
Average initial momentum $k_{Z_0}$ (atomic units)	7.349	7.349
Basis set parameters		
$N_z$	108	108
Grid spacing $\Delta Z$ (bohr)	0.25	0.25
Lattice parameter $a$ (Å)	2.84	2.84
Maximum value of $j$ in basis $j_{\max}$	6	6
Time propagation		
Size time step (atomic units)	1500	800
Number of time steps	30	56
Total propagation time $T$	45000	44800
Tolerance parameter $\text{tol}_{\text{ch}}$	$10^{-13}$	$10^{-13}$
Number of Hamiltonian operations $N_{\text{ham}}$	2250	3808
Optical potential		
Initial value of range $Z_1^{\min}$ (bohr)	22.75	22.75
Proportionality constant $A_2$ (hartree)	0.061	0.061
Range $L$ (bohr)	4.0	4.0
Other		
Analysis value of $Z, Z_{\infty}$ (bohr)	22.75	22.75
Time interval analysis $\Delta t_{\text{an}}$ (atomic units)	150	160
Tolerance norm elastic grid $\text{tol}_{\text{sp}}$	$10^{-10}$	$10^{-10}$
Number of grid points elastic grid $N_{Z^{\text{sp}}}$	128	128
Cut-off potential expansion $V_{\text{max}}^{\text{cut}}$ (eV)	0.6	0.9
Coefficient $c$ in Eq. (27)	1.4	2.0
Cut-off kinetic energy $T_{\text{cut}}$ (eV)	0.6	0.6

$k_{Z_0}$  given in Table II corresponds to a collision energy  $E_{\text{col}}$  of 0.2 eV, and all calculations were performed for normal incidence of the wave packet.

The Chebyshev method<sup>83</sup> was used to propagate the wave function in time. For both the CCWP and the SAWP method, the total propagation time and the number and size of the time steps used are given in Table II. The order of the Chebyshev expansions employed was taken such that the highest order Bessel expansion coefficient was less than the tolerance parameter  $\text{tol}_{\text{ch}}$  (see Table II). To avoid instabilities in the propagation due to the use of an optical potential, the time step was chosen small enough to ensure that the order of the Chebyshev expansion did not exceed 80. For both methods, we also give the values of  $V_{\text{max}}^{\text{cut}}$  and  $c$  required for convergence in Table II (see Sec. II D), and the total number of Hamiltonian operations  $N_{\text{Ham}}$  required for getting probabilities. For a discussion of these values, see Sec. III.

In all calculations, we use the empirical  $\text{H}_2$  rotational energies as obtained from Ref. 93, rather than treating  $\text{H}_2$  as a rigid rotor. All calculations presented here are for scattering of  $\text{H}_2$  from its  $j=0$  rotational state, and of course we only include rotational states with  $j$  is even in the basis sets. In the SAWP calculations, the  $A_2$  parameters given in Table II represent maximum values, and we obtain channel dependent optimal  $A_2$  values using linear interpolation of Table III of Ref. 62.

As discussed in Sec. II A, the calculation of  $S$ -matrix elements involves time to energy Fourier transforms of time-dependent coefficients computed at fixed time intervals  $\Delta t_{\text{an}}$  by projecting the wave function on asymptotic eigenstates at

an asymptotic value ( $Z_{\infty}$ ) of the scattering coordinate. To obtain correct results,  $\Delta t_{\text{an}}$  should be much smaller than the timestep used in the calculations (see Table II for the values used for  $\Delta t_{\text{an}}$  and  $Z_{\infty}$ ). As described in Ref. 84, obtaining the wave function at  $Z=Z_{\infty}$  at intermediate times presents no problem in case the Chebyshev algorithm is used. At any intermediate time, the wave function is obtained at  $Z=Z_{\infty}$  simply by using the Bessel expansion coefficients appropriate to that time. The procedure used involves no extra Hamiltonian operations,<sup>64</sup> and requires little overhead.

The model potential used in the present work is switched off smoothly in the range 20–22.75 bohr, using the function of Eqs. (10) of Ref. 94. In this range, the interaction potential is already quite small. The validity of the switching procedure was checked by also performing calculations in which the model potential acts over an even longer range of  $Z$ .

In the CCWP method, when performing the FFT's for a given rotational state the wave function is held in an array  $ar(nz, ny, nx)$ , where the first dimension is for  $Z$ , etc. The FFT's were performed consecutively using the scilib Cray routine CFFTMLT, vectorizing along  $Y$  and  $X$  when performing the FFT's in  $Z$ , vectorizing along  $Z$  when performing FFT's along  $Y$ , and vectorizing along  $Z$  and  $Y$  when performing FFT's along  $X$ . Care was taken to avoid memory bank conflicts. The 3D FFT routine CFFT3D is very inefficient for low values of  $N_x$  and  $N_y$ ,<sup>95</sup> but the efficiency of the algorithm outlined above and using CFFTMLT is comparable<sup>96</sup> to that of a sophisticated algorithm using rotations to obtain optimized vector lengths.<sup>95</sup>

Details in which the CCWP calculations and SAWP calculations differ are given in Sec. III.

### III. RESULTS AND DISCUSSION

In order to compare the performance of the CCWP and SAWP methods, first an accurate reference calculation was performed using the SAWP method. In this calculation, the potential expansion of Eq. (13) was used. In the potential expansion, we included diffraction terms with  $|m| \leq |n| \leq n_{\text{max}}^p = 3$ , and rotational terms with  $j$  up to 6. In the wave function expansion [Eq. (14)], diffraction terms were included such that  $|m| + |n| \leq O_w = 9$ , and rotational terms were included with  $j$  up to 6. No attempt was made to use the increased sparseness of the potential coupling matrix at longer range in the reference calculation. Tests were performed to ensure that the reference calculation converged all probabilities for rotationally and diffractively inelastic scattering from the  $j=0$  initial rotational state that are larger than  $10^{-4}$  to within less than 0.5%.

The next step was to perform CCWP and SAWP calculations, and to investigate to what extent one can take advantage of the sparseness of the potential coupling matrix at long range using the methods outlined in Secs. II B and II C. In performing these comparative calculations, we demand that the results agree with those of the reference calculation to within 1% for all probabilities larger than  $10^{-4}$ . The CCWP results are discussed in Sec. III A, and the SAWP results in Sec. III B. These sections focus on the improve-

TABLE III. Probabilities for rotationally and diffractively inelastic scattering  $P(00 \rightarrow jm_jnm)$  are given for five different calculations. Calculation A is an accurate reference calculation performed with the SAWP method, using  $n_{\text{max}}^p = 3$  and  $O_w = 9$ . Calculations B and C are CCWP calculations with  $N_x = N_y = 12$ . Calculations D and E are SAWP calculations in which  $n_{\text{max}}^p = 2$  and  $O_w = 8$ . In calculations C and E, the sparseness of the potential coupling matrix at longer range was used as outlined in Secs. II B and II C, using  $V_t = 3.2 \times 10^{-3}$  meV.

$j$	$m_j$	$n$	$m$	A(ref)	B(CCWP)	C(CCWP)	D(SAWP)	E(SAWP)	$j$	$m_j$	$n$	$m$	A(ref)	B(CCWP)	C(CCWP)	D(SAWP)	E(SAWP)		
0	0	0	0	0.8532(-2)	0.8526(-2)	0.8526(-2)	0.8536(-2)	0.8526(-2)	2	1	1	0	0.1457(-2)	0.1457(-2)	0.1456(-2)	0.1455(-2)	0.1454(-2)		
		1	0	0.1756(-1)	0.1756(-1)	0.1756(-1)	0.1757(-1)	0.1758(-1)			2	0	0.1606(-2)	0.1605(-2)	0.1605(-2)	0.1607(-2)	0.1606(-2)		
		2	0	0.4982(-2)	0.4986(-2)	0.4986(-2)	0.4989(-2)	0.4994(-2)			1	1	0.1551(-2)	0.1551(-2)	0.1551(-2)	0.1458(-2)	0.1546(-2)		
		1	1	0.1281(-1)	0.1281(-1)	0.1281(-1)	0.1281(-1)	0.1281(-1)			3	0	0.4642(-3)	0.4655(-3)	0.4654(-3)	0.4648(-3)	0.4643(-3)		
		3	0	0.2084(-2)	0.2080(-2)	0.2079(-2)	0.2084(-2)	0.2083(-2)			2	1	0.2492(-2)	0.2491(-2)	0.2491(-2)	0.2492(-2)	0.2492(-2)		
		2	1	0.2516(-1)	0.2516(-1)	0.2516(-1)	0.2516(-1)	0.2516(-1)			2	-1	0.2399(-2)	0.2398(-2)	0.2399(-2)	0.2400(-2)	0.2401(-2)		
		4	0	0.3715(-3)	0.3723(-3)	0.3722(-3)	0.3727(-3)	0.3725(-3)			3	1	0.1044(-2)	0.1045(-2)	0.1044(-2)	0.1044(-2)	0.1043(-2)		
		3	1	0.9240(-2)	0.9233(-2)	0.9233(-2)	0.9242(-2)	0.9239(-2)			3	-1	0.6177(-3)	0.6190(-3)	0.6192(-3)	0.6192(-3)	0.6188(-3)		
		2	2	0.3881(-1)	0.3882(-1)	0.3882(-1)	0.3879(-1)	0.3879(-1)			2	2	0.1062(-2)	0.1062(-2)	0.1062(-2)	0.1061(-2)	0.1061(-2)		
		4	1	0.9751(-3)	0.9792(-3)	0.9791(-3)	0.9764(-3)	0.9757(-3)			3	2	0.2853(-3)	0.2853(-3)	0.2853(-3)	0.2859(-3)	0.2855(-3)		
		3	2	0.1142(-1)	0.1141(-1)	0.1141(-1)	0.1140(-1)	0.1140(-1)			3	-2	0.2251(-3)	0.2258(-3)	0.2259(-3)	0.2252(-3)	0.2250(-3)		
		4	2	0.1001(-2)	0.1002(-2)	0.1001(-2)	0.1005(-2)	0.1004(-2)			2	2	1	0	0.2732(-2)	0.2732(-2)	0.2732(-2)	0.2737(-2)	0.2736(-2)
		3	3	0.2884(-2)	0.2881(-2)	0.2881(-2)	0.2889(-2)	0.2887(-2)					2	0	0.1687(-2)	0.1687(-2)	0.1686(-2)	0.1688(-2)	0.1688(-2)
		4	3	0.2026(-3)	0.2021(-3)	0.2021(-3)	0.2014(-3)	0.2013(-3)					1	1	0.2135(-3)	0.2135(-3)	0.2134(-2)	0.2135(-3)	0.2135(-3)
2	0	0	0	0.7331(-2)	0.7334(-2)	0.7336(-2)	0.7334(-2)	0.7333(-2)	3	0			0.2126(-3)	0.2127(-3)	0.2126(-3)	0.2123(-3)	0.2124(-3)		
		1	0	0.1887(-3)	0.1885(-3)	0.1886(-3)	0.1889(-3)	0.1887(-3)	2	1	0.4563(-2)	0.4563(-2)	0.4563(-2)	0.4561(-2)	0.4562(-2)				
		2	0	0.3729(-3)	0.3735(-3)	0.3734(-3)	0.3741(-3)	0.3739(-3)	2	-1	0.5923(-3)	0.5923(-3)	0.5922(-3)	0.5922(-3)	0.5924(-3)				
		1	1	0.8804(-2)	0.8804(-2)	0.8803(-2)	0.8803(-3)	0.8804(-2)	3	1	0.1888(-2)	0.1886(-2)	0.1886(-2)	0.1887(-2)	0.1886(-2)				
		3	0	0.3291(-3)	0.3276(-3)	0.3276(-3)	0.3287(-3)	0.3281(-3)	3	-1	0.3645(-3)	0.3636(-3)	0.3635(-3)	0.3643(-3)	0.3645(-3)				
		2	1	0.1364(-2)	0.1363(-2)	0.1363(-2)	0.1364(-2)	0.1364(-2)	2	2	0.1170(-2)	0.1170(-2)	0.1170(-2)	0.1172(-2)	0.1172(-2)				
		2	2	0.7215(-3)	0.7209(-3)	0.7207(-3)	0.7208(-3)	0.7211(-3)	4	1	0.1481(-3)	0.1489(-3)	0.1489(-3)	0.1482(-3)	0.1480(-3)				
		3	2	0.1510(-3)	0.1507(-3)	0.1507(-3)	0.1510(-3)	0.1511(-3)	3	2	0.9760(-3)	0.9756(-3)	0.9757(-3)	0.9756(-3)	0.9751(-3)				
									3	3	0.1025(-3)	0.1022(-3)	0.1022(-3)	0.1025(-3)	0.1023(-3)				
									0	0	sum	0.7110(0)	0.7109(0)	0.7109(0)	0.7109(0)	0.7110(0)			
							2	0	sum	0.6214(-1)	0.6214(-1)	0.6213(-1)	0.6215(-1)	0.6215(-1)					
							2	1	sum	0.5367(-1)	0.5368(-1)	0.5368(-1)	0.5366(-1)	0.5365(-1)					
							2	2	sum	0.5938(-1)	0.5937(-1)	0.5937(-1)	0.5939(-1)	0.5939(-1)					

ments obtained using the increased sparseness of the potential matrices at longer range.

The performance of the CCWP and SAWP methods is compared in Sec. III C. In this section, we also speculate on the efficiency of a CCWP method using symmetry and the efficiency of using different representations at different ranges of the scattering coordinate, using a mixed scheme. We will also briefly discuss the potential usefulness of the SAWP method for performing 6D calculations on dissociative chemisorption of  $H_2$  on a surface of square lattice symmetry, like the Cu(100) surface, in the context of such a mixed scheme.

### A. CCWP results

To obtain converged results using the CCWP method, it was necessary to use 12 grid points along  $X$  and  $Y$  ( $N_x = N_y = 12$ ). This corresponds to using a square diffraction basis containing 144 states. In the rotational basis set, channels with  $j$  up to 6 were required for convergence ( $N_{\text{rot}} = 28$ ). The spectral basis effectively used in the CCWP calculations therefore contained 4032 rotation-diffraction states.

In Table III, results of two different CCWP calculations are compared with the results of an accurate reference calculation. In one calculation (CCWP B) we do not attempt to exploit the sparseness of the potential coupling matrix. The

potential expansion used in the calculation contained spherical harmonics with  $j$  up to 6 (see also Sec. II E), and the resulting potential coupling matrix was full, only 13% of the matrix elements being zero over the entire range of the scattering coordinate. Test calculations showed that in the potential expansion spherical harmonics should be included with  $j$  up to 6 in order to get converged results.

In the other calculation (CCWP C) we did take advantage of the sparseness of the potential coupling matrix. In this calculation, we neglected matrix coupling elements once their absolute value became larger than a threshold value  $V_t$  at larger values of  $Z$  (see Sec. II B for the exact method used) in the matrix-vector multiplications corresponding to the potential energy operation on the wave function. Trial calculations in which we increased the threshold value  $V_t$  by a factor  $10^{0.5}$  in subsequent calculations showed that for convergence  $V_t = 3.2 \times 10^{-3}$  meV was required.

The CPU times and central memory requirements of the CCWP calculations are compared in Table IV. As can be seen from this table, exploiting the increase in the sparseness of the potential coupling matrix with increasing scattering coordinate leads to a large reduction in the CPU time required for the potential energy operation and the amount of central memory required to hold the potential coupling matrix on the grid in  $X$ ,  $Y$  and  $Z$  (by a factor 4.5 in both cases).

TABLE IV. CPU times (in CPU s) and central memory requirements (in Mw) are given for four different calculations. Calculations B and C are CCWP calculations with  $N_x=N_y=12$ . Calculations D and E are SAWP calculations in which  $n_{\max}^p = 2$  and  $O_w=8$ . In calculations C and E, the sparseness of the potential coupling matrix at longer range was used as outlined in Secs. II B and II C using  $V_t=3.2\times 10^{-3}$  meV. The calculations were performed on a Cray Y-MP C98.

	CCWP(B)	CCWP(C)	SAWP(D)	SAWP(E)
CPU times				
Chebyshev algorithm	42.9	43.0	8.8	8.9
K, FFt's along Z	102.1	101.8	22.4	22.6
K, FFt's along X and Y	100.6	101.8	0	0
K, multiplications	6.9	6.8	2.4	2.4
V	459.2	101.9	878.5	146.4
Rest	41.8	42.4	11.8	13.7
Total	753.5	396.1	923.9	194.0
Memory requirements				
V, arrays	<0.01	0.06	0.17	4.69
V, matrix elements	9.4	2.1	2.6	1.1
Storage arrays wave function	4.4	4.4	0.46	0.46
Total	14.5	8.0	4.3	8.1

The total CPU time is reduced by a factor 1.9, and total memory usage by a factor 1.8. We expect even larger gains in efficiency for cases in which more rotational states are necessary to describe the scattering, like the scattering of  $N_2$  from LiF.<sup>16,59</sup> We also expect that our adaption of the CCWP method will make it competitive with the FBWP method of Lemoine and Corey<sup>58,59</sup> mentioned in Sec. I. We hope to carry out a comparison of the efficiency of the CCWP and FBWP methods for the present model system and for  $N_2$ +LiF in the near future.

## B. SAWP results

In performing SAWP calculations, we first checked whether it is best to use a square diffraction basis in the calculations [such that, in the wave function expansion of Eq. (14),  $|m| \leq |n| \leq n_{\max}^w$ , where  $n_{\max}^w$  is the maximum value of  $m$  and  $n$  in the basis set] or a diamond shaped basis set (such that  $|m|+|n| \leq O_w$ , where  $O_w$  is the maximum diffraction order in the basis set). It was found that the use of a diamond shaped diffraction basis set was cheaper. For converged results, it is necessary to use either  $O_w=8$  (diamond shaped basis) or  $n_{\max}^w = 6$  (square basis). Using  $j_{\max}=6$  in the rotational basis, the rotation-diffraction basis set then contains 534 functions when using the diamond shaped basis and 618 functions in case the square basis is used.

For the potential expansion the opposite was found to be true. Converged results are obtained in case diffraction terms are retained in the potential expansion such that  $|m| \leq |n| \leq n_{\max}^p = 2$ . In contrast, a diamond shaped basis for the potential expansion functions required  $|m|+|n| \leq O_p=4$ . Using  $j_{\max}=6$  in the potential expansion, the number of symmetry adapted rotation-diffraction functions is 98 in case the square basis is used, and 158 in case the diamond shaped basis was used.

In Table III, we compare the results of two different SAWP calculations with the results of the reference calculation.

The two calculations use the same rotation-diffraction basis set in the wave function ( $j_{\max}=6$ ,  $O_w=8$ ) and the same parameters for the potential expansion ( $j_{\max}=6$ ,  $n_{\max}^p = 2$ ). The resulting symmetry adapted basis set contains 534 states, whereas a nonsymmetry adapted basis set would contain  $[O_w^2 + (O_w + 1)^2] \times N_{\text{rot}} = 4060$  states ( $N_{A_1}/N = 7.6$ , which is close to 8). In the SAWP D calculation, we do not use the increased sparseness of the potential coupling matrix at longer range, though we do take advantage of matrix coupling elements being zero over the entire range of  $Z$ . Of course, this is the case if the integrals over the states that are coupled and the potential expansion functions are zero for all expansion functions [see Eqs. (13) and (15)], and this was true for approximately 50% of the potential coupling matrix elements. In the SAWPE calculation, in addition the nonzero coupling matrix elements are neglected once at long range their absolute value becomes less than  $V_t$ , using the procedure described in Sec. II C. Trial calculations similar to the ones performed before using the CCWP method showed that for convergence the same value of  $V_t$  was required ( $3.2 \times 10^{-3}$  meV).

Memory requirements and CPU times are compared for the two SAWP calculations in Table IV. As can be seen, employing the increased sparseness of the potential coupling matrix at long range leads to a large reduction of the CPU time spent on performing the potential energy operation (by a factor of 6). Because most of the total CPU time in the SAWP method is spent in performing the potential energy operation, the total cost of the calculation is also greatly reduced (by a factor of 4.75). However, the less expensive calculation now requires more memory. The increase in memory is mostly due to reserving space for an array which keeps track of which coupling matrix elements are important in the part of the potential matrix multiplication which is vectorized over states and performed at short range only.

In the SAWPE calculation, the multiplication with the diagonal potential matrix elements was vectorized over  $Z$ . Of the off-diagonal nonzero matrix elements, roughly 10% are important for 15 or more grid points in  $Z$  (in the range 3.5–7.0 bohr and beyond) and, for these matrix elements, the multiplication was vectorized over  $Z$ , the associated computational cost being roughly 38% of the total time required for the potential energy operation. The multiplication with off-diagonal matrix elements which are only important in the range 3.5–6.75 bohr was done vectorising over states. The use of the mixed vectorising scheme is essential for obtaining the large reduction in CPU time for performing the potential energy operation: A reduction factor of only 1.8 would have been achieved if all multiplications would have been performed vectorising over  $Z$ , which is to be contrasted to the factor of 6 achieved using the mixed scheme.

## C. Comparison of the methods

To compare the performance of the CCWP and SAWP methods in terms of CPU time usage and memory requirements, we again refer to Table IV. In terms of CPU time, the CCWP method is slightly more efficient than the SAWP method if the sparseness of the potential coupling matrix at

longer range is not used, though it requires much more memory. On the other hand the SAWP method is faster than the CCWP method by a factor of 2 if the increased sparseness at longer range is used, while requiring roughly the same amount of memory for this case.

In previous work,<sup>63</sup> we compared the efficiency of the CCWP and SAWP methods for the  $\text{H}_2+\text{LiF}(001)$  model problem using the Wolken potential.<sup>66</sup> In those calculations, we found the SAWP method to be faster by a factor of 9. Given that result, the performance of the SAWP method for the present model potential is somewhat disappointing. Whether the SAWP method will be more efficient than the CCWP method and by how much in the end depends on a trade-off: For any particular problem, the SAWP method will be more efficient if gains made by performing the kinetic energy operation are not offset by losses incurred in performing the potential energy operation less efficiently.

The absolute increase in computational cost of the potential energy operation (in going from CCWP to SAWP) depends on (i) the extent to which the cost associated with the potential energy operation dominates the total computational cost in the CCWP method and (ii) the extent to which this cost is further increased by switching from the CCWP method to the SAWP method. The relative cost of the potential energy operation depends on the size of the rotational basis set ( $N_{\text{rot}}$ ) and the average number of rotational states a given rotational state is coupled to in the potential coupling matrix ( $N_{\text{coup}}^{\text{rot}}$ ). The factor by which the cost of the potential energy operation increases is determined by the average number of diffraction states a given diffractive state is coupled to in the SAWP method ( $N_{\text{coup}}^{\text{dif}}$ ). Reasons that the SAWP method is more expensive than the CCWP method for the present model problem (if no use is made of increased sparseness of the potential coupling matrix at longer range) while the reverse was true<sup>63</sup> for the Wolken potential<sup>66</sup> are (i) for the present ( $\phi$  dependent) model potential, the relative cost of the potential energy operation in the CCWP method is much larger (61%) than for the Wolken potential (9%), because a larger rotational basis set is required ( $N_{\text{rot}}=28$  instead of 6) and because the larger potential expansion on average couples more rotational states with one another ( $N_{\text{coup}}^{\text{rot}}=24.5$  instead of 2.5) and (ii) in going to the SAWP method, the cost of the potential energy operation increases by a larger factor because the larger potential expansion on average couples more diffractive states with one another (upperbounds are  $N_{\text{coup}}^{\text{dif}}=25$  for the model potential, instead of 5 for the Wolken potential<sup>63</sup>).

An additional reason for the decreased efficiency of the SAWP method for the model potential used in the present work was discussed in Secs. II D and II E. The inclusion of the electrostatic interaction in the model potential leads to a larger spectral range, the problem being most severe for the SAWP method. As can be seen from Table II, as a result fewer Hamiltonian operations (by a factor of 1.7) are required in the CCWP calculations. In the previous calculations on the Wolken potential, roughly the same number of Hamiltonian operations was required in both methods.

The net result is that the potential energy operation becomes more expensive in the SAWP method than in the

CCWP method. According to the scaling relations and taking into account the effect of the increased spectral range, the potential energy operation would be expected to become more expensive by a factor no larger than 2.8 in changing to the SAWP method. Because the average number of diffraction states a given diffraction state will couple to is less than the upperbound  $N_{\text{coup}}^{\text{dif}}$ , the scaling of the potential energy operation is not as severe, and the potential energy operation in the SAWP method is only more expensive by a factor 1.9 in the calculations not employing sparseness at longer range. Because the potential energy operations dominate the computational cost (61%) also in the CCWP method if sparseness at longer range is not used, the SAWP method is more expensive in this case (by a factor 1.2), though requiring much less central memory (by a factor 3.4).

If the increased sparseness of the coupling matrix at longer range is used, the potential energy operations no longer dominate the total computational cost of the CCWP method (only 26%, see Table IV). As a result, it now becomes favorable to change to a method in which the evaluation of the potential energy operation is more expensive, but the kinetic energy operation is less expensive, the SAWP method now being cheaper by a factor 2. If the sparseness at longer range is used, the potential energy operations are more expensive by only a factor 1.4 in the SAWP method, compared to a factor 1.9 if sparseness at longer range is not used. This is probably a result of the potential expansion coefficients [Eq. (13)] decreasing fast with increasing molecule-surface distance for expansion functions which are of high diffraction order.

In the CCWP calculations that we present, symmetry was not used. However, it should be possible to implement the use of symmetry also in the CCWP method, by only expanding the wave function on symmetry needed points in  $x$  and  $y$ .<sup>57,59</sup> For the present example ( $m_j=0$  initially, the total wave function has  $A_1$  symmetry) it is only necessary to use points with  $0 \leq x \leq a/2$  and  $0 \leq y \leq x$ , resulting in 28 symmetry needed points rather than 144 as used here.<sup>59</sup> In a method which we will call the "SNWP" method (SNWP for symmetry needed close-coupling wave packet method) the potential energy operation would be performed only on the symmetry needed points, and likewise for the FFT's along  $Z$  required for performing the kinetic energy operation, resulting in savings by a factor of  $144/28$  (5.1). One way to perform the transformations to momentum space along  $X$  and  $Y$  is to first expand the wave function on the full  $x, y$  grid (144 points) and then perform FFT's along  $x$  and  $y$ .<sup>59</sup> Using this procedure, there would still be a saving in performing the transformations along  $x$  and  $y$  relative to the cost involved in the CCWP method (by a factor 1.7 for the present example), because the FFT's along  $x$  need only be performed for  $0 \leq y \leq a/2$  and vice versa for the FFT's along  $y$ .<sup>59</sup> The entire scheme discussed here is completely analogous to the scheme already used successfully by Lemoine in FBWP calculations on  $\text{N}_2+\text{LiF}$  using a model potential.<sup>59</sup>

Estimates of the computational costs of the SNWP method are compared with the costs of the CCWP and SAWP methods for the case that the increased sparseness of the potential coupling matrix at longer range is used in Table

TABLE V. CPU times (in CPU s) and central memory requirements (in Mw) are given for four different calculations. The first two calculations are the CCWP(C) and SAWP(E) calculations of Table IV. Under "SNWP," we give the estimated cost of a CCWP calculation that would employ symmetry by only propagating symmetry-needed diffraction states. Under "mixed," we give the estimated cost of a calculation using a mixed approach (see also the text). The (estimated) costs are for a Cray Y-MP C98.

	CCWP(C)	SAWP(E)	SNWP	Mixed
CPU times				
Chebyshev algorithm	43.0	8.9	8.3	5.3
$K$ , FFt's along $Z$	101.8	22.6	19.9	13.3
$K$ , FFt's along $X$ and $Y$	101.8	0	59.2	15.3
$K$ , multiplications	6.8	2.4	1.4	1.4
$V$	101.9	146.4	19.8	47.8
Rest	42.4	13.7	20.0	12.0
Total	396.1	194.0	128.6	95.1
Memory requirements				
$V$ , arrays	0.06	4.69	0.06	0.1
$V$ , matrix elements	2.1	1.1	0.41	0.6
Storage arrays wave function	4.4	0.46	0.9	0.6
Total	8.0	8.1	1.4	1.3

V. The estimated costs of the operations in the SNWP method have been obtained by dividing the costs of the operations of the CCWP method by a factor 5.14, except for the cost of transforming along  $x$  and  $y$  (a factor 1.7) and the overhead (simply a rough estimate, there should be additional costs for expanding the wave function on the full grid in  $x$  and  $y$  prior to transforming along  $x$  and  $y$ ). As can be seen from the table, the estimated cost of the SNWP method is actually less than that of the SAWP method. Similarly, the SNWP method would require less memory. Obviously, this then calls into question the usefulness of the SAWP method. However, a number of considerations show that the SAWP method may in fact still be quite useful.

For one thing, it is not clear whether the savings predicted for the SNWP method would actually be achieved in calculations on machines with vector processing capabilities. For instance, the vector length that would be achieved in performing the potential energy operation using the scheme discussed in Sec. II B would be less optimal (28) than in the CCWP method (144, the optimal vector length on the Cray is 64 or "a lot more"). We still have to establish how well the SNWP method would work in practice for the model problem presently under consideration, which we hope to do in the near future.

Second, it may still be favorable to combine the SAWP method (used at long range) with the CCWP or FBWP method (used at short range and employing symmetry). Presently, most of the CPU time spent in performing the potential energy operation in the SAWP method goes to performing this operation at short range (62%, for  $Z < 7a_0$ ). It may therefore well be favorable to use a scheme in which a symmetry adapted full close-coupling representation is used at large molecule-surface distances and a hybrid (CCWP) or full FBR (FBWP) representation is used for the  $x$ ,  $y$ ,  $\theta$ , and  $\phi$  coordinates close to the surface. Using such a scheme, larger time steps can be taken than in the SAWP only scheme, because it is easier to place an upper bound on  $V$  close to the

surface using the hybrid representation, and much easier to do so in the FBWP method, in which the potential energy operation is performed in coordinate space.

The estimated cost of a mixed (SNWP at short range, SAWP at long range) scheme is also given in Table V, and compared to that of the SAWP only (actual costs) and SNWP only (estimated costs) schemes. In the mixed scheme, the momentum representation is used as the primary representation for the  $x$ ,  $y$ ,  $\theta$ , and  $\phi$  degrees of freedom. The potential energy operation is performed by matrix multiplications for  $Z \geq 7a_0$  (SAWP) and by performing transforms along  $x$  and  $y$  and (smaller) matrix multiplications at smaller values of  $Z$  (SNWP). The time-step used is that used in the SNWP or CCWP scheme. As can be seen from Table V, the mixed scheme is expected to be cheaper. However, the same caveat applies as that given before in discussing the SNWP estimates: It is not clear beforehand whether optimal vector lengths can be achieved in the mixed scheme and, therefore, what the actual performance of such a scheme will be on a machine like the one presently used (a Cray Y-MP C98).

As mentioned in Sec. I, the use of symmetry is relevant to performing high dimensionality calculations on reactive scattering of molecules at surfaces. Many dissociative chemisorption problems (in particular, the  $H_2 + Cu$  benchmark system) obey normal energy scaling, meaning that to a good approximation the dissociation probability only depends on the kinetic energy normal to the surface. This means that the multidimensional DFT (density functional theory) potential energy surfaces now being developed for  $H_2$ +low index copper surfaces<sup>80-82</sup> can in principle be tested by performing wave packet calculations for normal incidence only, ideally modeling all molecular degrees of freedom. Compared to the five-dimensional (5D) inelastic scattering problem discussed here, one more degree of freedom ( $r$ , the H-H distance) would need to be added, resulting in a six-dimensional (6D) problem.

A complication that should occur in 6D calculations is that many rotational states should have to be included in the basis set, because the rotational constant of the molecule decreases as it dissociates. As a result, the calculations should be quite expensive and require much central memory, and 6D wave packet calculations on dissociative chemisorption have not yet been reported. Employing symmetry in calculations on normal incidence would reduce both CPU time and central memory requirements. In this context, we expect the SAWP method discussed here to be useful, provided it is used in a mixed scheme. Problems with imposing a maximum on the potential coupling matrix using a close coupling representation should be especially severe for dissociative reactive scattering for some combinations of  $Z$  and  $r$ , especially in case  $Z$  is small and  $r$  is large where, in perpendicular orientations, the molecule will point one of its atoms into the surface. It is anticipated that using the FBWP representation for such combinations of  $Z$  and  $r$  should help much to increase the efficiency of a mixed scheme.

#### IV. CONCLUSIONS

We have used the  $H_2 + LiF(001)$  system to test the performance of two wave packet methods on a molecule-



surface system of fairly high corrugation. A new,  $\phi$ -dependent model potential was used. The potential used yields a good description of the most important aspects of the system under investigation, like the increased anisotropy and corrugation close to the surface and the anisotropy associated with the long range interaction. The comparison extends previous work which was done using a  $\phi$ -independent model potential due to Wolken, which contains only a few anisotropic and corrugation expansion terms.

In both wave packet methods investigated, a close-coupling or variational basis set representation (VBR) was used for some or all degrees of freedom other than the scattering coordinate. In the close-coupling wave packet (CCWP) method, a grid representation is used for the diffractive degrees of freedom, while the VBR is used for the rotational degrees of freedom. In the other method (SAWP for symmetry adapted full close-coupling wave packet method), a full close-coupling representation is employed for the  $x$ ,  $y$ ,  $\theta$ , and  $\phi$  degrees of freedom, also taking advantage of the special symmetry relations that exist for normal incidence. Both methods were tested for a collision energy of 0.2 eV with  $H_2$  at normal incidence in the initial  $j=0$  rotational state.

We have shown that for both methods large savings in CPU time can be achieved by taking advantage of the increased sparseness of the potential coupling matrix at larger values of the scattering coordinate. The schemes introduced here reduced the cost of the potential energy operation by a factor of 4.5 in the CCWP method, and by a factor of 6 in the SAWP method. Increasing sparseness of the potential coupling matrix at longer range should be a general feature in scattering problems. Therefore, schemes like those introduced here should be effective also in bringing down the cost of wave packet methods that deal with other scattering problems, but also employ a close-coupling representation for at least some degrees of freedom.

For the model problem under investigation, the SAWP method was faster than the CCWP method by a factor of 2 provided that the increased sparseness of the potential coupling matrix at longer range was employed. On the other hand, the SAWP method is expected to be less efficient than a symmetry adapted version of the CCWP method in which only symmetry-needed diffraction states are propagated. Nevertheless, we expect the SAWP method to be useful in a mixed scheme which would employ different representations over different ranges of the scattering coordinate. A scheme which we expect to be optimal employs a finite-basis representation (FBR) or a hybrid representation at short range (the FBWP or finite basis wave packet method of Lemoine and Corey, or the CCWP method) while employing the full close-coupling representation at longer range, using symmetry in both cases. This scheme would combine the advantages of a FBR of hybrid method (smaller spectral range, potential energy operation is less expensive at short range where the potential coupling matrix would be full for a method employing a full close-coupling representation) with the advantages of the SAWP method (transforms along  $x$ ,  $y$ ,  $\theta$ , and  $\phi$  can be avoided, and the potential energy operation is efficient at long range because the potential matrix is sparse at long

range). We expect that such a scheme would be highly useful in performing six-dimensional (6D) wave packet calculations on the benchmark problem of dissociative chemisorption of  $H_2$  on low index copper surfaces, for which normal energy scaling is observed. Such calculations would constitute important tests of the multidimensional potential energy surfaces that are now being developed for the  $H_2$ +Cu system using density functional theory.

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